



Short communication

Designing lead–acid batteries to meet energy and power requirements of future automobiles[☆]Patrick T. Moseley^{a,*}, David A.J. Rand^b, Boris Monahov^a^a Advanced Lead–Acid Battery Consortium, ILZRO, 1822 East NC Highway 54, Suite 120, Durham, NC 27713, USA^b CSIRO Energy Technology, Box 312, Clayton South, Victoria 3169, Australia

H I G H L I G H T S

- ▶ New light on the processes that limit the life of lead–acid batteries.
- ▶ Particularly in high-rate partial-state-of-charge operation.
- ▶ The paper outlines remedies for those processes.

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A B S T R A C T

A review is given of the factors that mitigate against the successful use of lead–acid batteries in the high-rate partial-state-of-charge (HRPSoC) duties experienced in hybrid electric vehicles, together with a consideration of successful remedies for those factors.

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1. Toward sustainable road transport

The design of automobile electric systems is currently undergoing a major change. The prime motivation for such action is the rapidly emerging legislation in many parts of the world to limit allowable fleet-wide emissions of carbon dioxide, CO₂, under pain of serious financial penalties for non-compliance. The imposed targets are often presented in terms of the quantity (grams) of CO₂ that may be emitted per kilometer driven. In Europe, the emission limits are 130 and 95 g per km by 2015 and 2020, respectively. The targets in the USA differ somewhat from those in Europe and may alternatively be quoted in terms of the Corporate Average Fuel Economy (CAFE) objectives; the Obama Administration in 2011 proposed 54.5 miles per gallon (US) by 2025.

It is anticipated that the first rank of targets can be met by introducing ‘stop–start’ vehicles. Consequently, and following the lead of BMW in 2009, all major car companies have plans in place to introduce, or in fact have already launched, such technology. With these vehicles, it is expected that a reduction in emissions of around 6% can be achieved, and this improvement could be extended to about 8% if regenerative braking were to be included.

2. New challenges for automotive batteries

Within a few years, new automobiles with only starting, lighting and ignition (SLI) battery functions will be in the minority. The battery in a stop–start vehicle, like that in hybrid electric vehicles (HEVs), must perform a duty that is far more demanding than the ‘traditional’ provision of energy for SLI operations. A stop–start vehicle, in which the engine shuts down whenever the vehicle becomes stationary, must be capable of performing during its designed lifetime perhaps ten times as many engine-cranks as

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its conventional predecessor. To support this extra drain on the battery and the considerable additional electric functionality that enables HEVs to provide launch-assist and, in some cases, limited electric-only propulsion, there is strong interest in the capture of regenerative braking energy. That is, the recovery of some fraction of the kinetic energy normally dissipated during braking of a vehicle and its return to the battery. For this mode of operation to be implemented successfully, the battery must operate in a 'high-rate partial-state-of-charge' (HRPSoC) regimen: 'high-rate' because energy from vehicle braking accrues at very high rates, and 'partial-state-of-charge' because the battery must be ready to accommodate charge whenever it becomes available. Unfortunately, lead–acid batteries that have been developed over decades to provide stellar performance in the provision of the SLI functions fail extraordinarily quickly when exposed to HRPSoC duty. Clearly, therefore, the shift in technology toward stop–start vehicles and HEVs poses major challenges for the lead–acid battery. These challenges, summarized in Table 1, are examined below in more detail, together with an explanation of the associated terminology.

During engine cranking in a conventional automobile, it has always been incumbent upon the SLI battery to deliver discharge currents of short duration — in Table 1, these currents are shown as 15 times the 1-h rate ($15 C_1$). By contrast, replacement of the charge used in cranking occurs at a modest rate; namely, at around the 1-h rate ($1 C_1$). The ultimate failure modes of SLI batteries are sufficiently understood and well managed so that most car batteries are now able to provide four-to-six years of service in temperate climates. In HEVs, including all stop–start vehicles that make use of regenerative braking, the batteries are subject to HRPSoC operation. Medium- and full-hybrids additionally operate with power-assist capability and therefore employ high-voltage battery packs (up to 150 V and over 200 V, respectively) that can experience very high rates of charge, e.g., up to $30 C_1$, see Table 1. Exposure to such events, albeit briefly, gives rise to a new failure mode that is manifest as an accumulation of lead sulfate at the negative plate, in particular on its surface [1,2]. This mechanism is less severe for micro-hybrids, which retain the use of 12 V batteries, since, even when they deploy regenerative braking, the charge rates may reach only 3–5 C_1 .

3. High-rate partial-state-of-charge operation

The origins of the processes that can lead to the early accumulation of lead sulfate on the negative plate of a lead–acid battery that is exposed to in HRPSoC schedules have been intensely studied in recent years. The key characteristics of battery duty in HEVs are as follows.

- Operation at a partial state-of-charge (PSoC) in order to allow the battery to accept charge from regenerative braking at all times.

- A virtually continuous series of 'micro-cycles', i.e., charge and discharge events that involve only a small fraction (typically 1–2%) of the battery's capacity.

In connection with the first of these characteristics, it is useful to note that at 'normal' rates of operation lead–acid batteries perform well within a PSoC range [3]. The common failure modes of grid corrosion and active-material shedding suffered by the positive plate are not aggravated in this mode of operation as is the case when deep cycling a battery from a full SoC. The data given in Table 2 provide an indication that a valve-regulated lead–acid (VRLA) battery cycled from top-of-charge provides approximately the same amount of energy throughput before failure irrespective of whether it is cycled down to 90, 60 or 20% SoC. By contrast, when the battery is cycled over a PSoC range (from 40 to 70% SoC and back), the total energy throughput is far greater. Thus, the search for the failure mode should focus on the 'high-rate' part of the HRPSoC operation, rather than on the 'partial-state-of-charge'.

The accumulation of lead sulfate on the negative plate during HRPSoC operation is attributed to inadequate charge acceptance [1]. In micro-hybrid duty, it is important to understand that the charge acceptance is not the neat and tidy process that may occur during routine battery cycling in a laboratory. Under vehicle conditions, the measurement of charge acceptance will be preceded by a rest period, a partial charge, or a partial discharge. Consequently, the recorded value may be well below that obtained from a systematic laboratory procedure. The real-world process has become known as 'dynamic charge acceptance' (DCA), and is defined [4] as: 'the amount of charge that is actually delivered to the battery during regenerative braking phases of a driving cycle, divided by the total amount of charge that theoretically could have been provided by the generator during such events'. In the first generation of stop–start vehicles, the DCA achieved is rather poor.

To understand why exposure to HRPSoC operation leads to poor DCA, it is important to focus on the fundamental processes that enable recharge of the lead–acid cell. The overall reaction proceeds via the so-called 'dissolution–precipitation mechanism', as expressed schematically in Fig. 1. The charge reaction at the negative plate depends, inter alia, on a sufficiently large reactive surface area and on adequate fluxes of sulfate ions, protons and lead ions to the surface, and of bisulfate ions (HSO_4^-) away from it, in order to sustain the charge current.

The individual micro-cycles experienced in normal HEV operation generally involve only a small fraction of the capacity of the battery, but they do take place at rather high rates. Thus they predominantly involve ions from solution that is very close to the reaction site on the solid surface. The rates at which charge and discharge events can proceed do, of course, depend directly on the available surface area of lead sulfate, and hence inversely on its crystallite size. The rate of charge is also limited by the solubility of lead sulfate and this, in turn, is controlled by the local acid concentration [5].

Table 1
Typical battery functions and failure modes in starting, lighting and ignition (SLI) and high-rate partial-state-of-charge (HRPSoC) duties.

Duty	SLI	HRPSoC
Vehicle	Conventional automobile	Hybrid electric vehicle
Range of state-of-charge	80–90%	50–70 or 70–90%
Maximum normal discharge rate	$15 C_1$	$15 C_1$
Maximum normal charge rate	$1 C_1$	$30 C_1$
Life-limiting mechanisms	Corrosion, shedding	Negative plate sulfation

Table 2
Energy delivered by batteries under traditional cycling and partial-state-of-charge cycling [3].

Operating regime	Number of cycles achieved	Total energy throughput, Ah
10% Depth-of-discharge	6000	86,000
40% Depth-of-discharge	1250	71,500
80% Depth-of-discharge	700	80,000
Partial state-of-charge (40–70% SoC)	5500	235,950

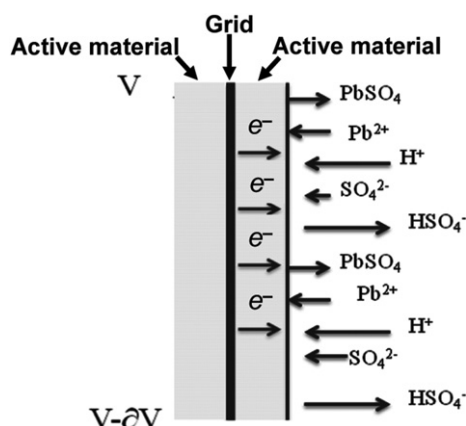


Fig. 1. Fluxes necessary to support charging of the negative plate (one side of plate only shown). The drop in potential down the height of the grid is indicated by the symbols V and $V-\delta V$.

During the normal discharge process of the lead–acid cell acid immediately adjacent to the plate surface is consumed, the local concentration of acid decreases, and the solubility of sulfate increases. Recharge immediately after a partial discharge is thus favored by the increase in solubility. With further charging, however, the concentration of acid close to the surface is increased, the solubility of lead sulfate is decreased, and the efficiency of recharge is impaired. Both sets of circumstances can be expected to be transitory as the acid concentration will eventually tend to be homogenized by diffusion. In the case of small micro-cycles, however, only the acid contained within the pores of the active material is involved in the depletion or concentration processes and diffusion into and out of the deepest pores may not be a rapid process. There are also indications from detailed analyses of Peukert plots [6] that, whereas acid depletion limits capacity at low rates of discharge, diffusion of bisulfate ions to the lead surface is the controlling factor at high rates.

Both the solubility of lead sulfate and the diffusion of ions within the electrolyte are enhanced with increasing temperature. Therefore, it is not surprising that dynamic charge acceptance has been found to improve with increase in temperature [7].

If the flux of protons to the reaction site, or the flux of bisulfate ions away from it, is insufficient, the potential will rise to a point where other reactions (viz., hydrogen evolution and/or the reduction of oxygen in VRLA batteries that has transferred from the positive plate) can accommodate some, or all, of the charge current. Lead sulfate will then not be removed and will accumulate. It is important to recognize that the accumulation of lead sulfate by this process is confined to the negative plate of the cell.

4. The role of grid resistance

In the discussion above, emphasis has been placed on the importance of the fluxes of reactant species that are necessary to maintain the charge reaction at high rates. Nevertheless, as indicated in Fig. 1, electrons are also essential participants in the reactions. On charging, the electrons exit the positive plate and enter the negative plate via a 'tab' and are then supplied to the respective active material via an embedded current-collector, the 'grid'. During either charge or discharge of a battery, a gradient of potential develops between the tab and the remote corners of the grid in each of the two plate polarities due to the resistance of the grid. At normal rates of charge or discharge, this gradient does not exert any significant effect on the performance of

the plate (and the cell of which it is part). At a high discharge rate, however, studies [8–12] have shown that non-uniformity of the potential can seriously limit the performance of the negative plate on discharge. It is not unreasonable to suppose that the grid resistance also adversely affects the charge process, especially at the rates that are involved in HRPSOC operation, which can be double those experienced in the charge events (cranking) that were the concern of the earlier studies [8–12].

A consideration of the current–potential plot for the cell reaction, as shown schematically in Fig. 2 serves to illustrate why the spread of potential is important. If the potential across the grid is not uniform, then only part of the grid will reside at the ideal potential for the charge reaction, which converts lead sulfate to lead. The remainder of the grid (and active material) will either be at an insufficiently negative potential for recharge or will be at too negative a potential such that hydrogen will be evolved at a significant rate.

Obviously, therefore, any change to the plate design that suppresses the influence of grid resistance will be beneficial. A good example is the incorporation of a second current tab located at the bottom of the plate and placed symmetrically opposite the normal one. When plates are connected using both tabs, HRPSOC performance can be boosted by two orders of magnitude [13].

5. Why only the negative plate?

The accumulation of lead sulfate that leads to early failure of lead–acid cells under HRPSOC operation occurs only on the negative plate. It should be instructive, however, to seek an understanding of why the mechanism by which this occurs (described in [5]) is not matched by a similar process on the positive. This may be due to the fact that, typically, the positive plate has a much higher double-layer capacitance (up to 70 F Ah^{-1}) than does the negative plate (up to 1.0 F Ah^{-1}) [14], and thereby has a greater ability to absorb short, sharp charge pulses. The higher capacitance of the positive plate is doubtless due in part to the fact that the positive active-material (PAM) generally exhibits a surface area that is up to four times larger than that of the negative active-material (NAM). Additionally, however, the processes that take place at the two surfaces are also likely to be different. For instance, whereas protons participate in the regular charge process at the surface of the NAM, it is water molecules that are involved at the surface of the PAM.

There has been considerable conjecture about the origins of the electrochemical capacity of the PAM. At one time, it was thought that only lead dioxide prepared electrochemically could provide

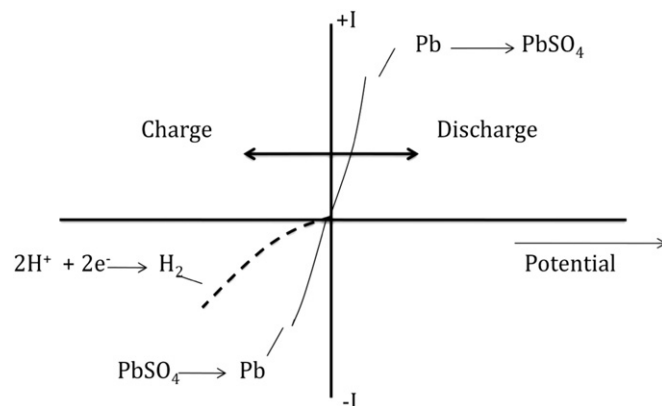


Fig. 2. Current–potential characteristics of the negative electrode in a lead–acid cell.

significant discharge capacity [15], but this was later shown not to be the case by a demonstration of discharge capacity from β -PbO₂ that had been prepared chemically by reacting red lead (Pb₃O₄) with nitric acid [16]. Inelastic neutron scattering studies [17] did, however, show that 'electrochemical' β -PbO₂ contained a significant quantity of hydrogen that was probably bound as water molecules at external surfaces of oxide crystals, whereas the 'chemical' variety contained no such hydrogen. Further work on the PAM [18] led to the suggestion that part of the material on the positive plate was gel-like, with no long-range-order, and the remainder of the oxide had the regular tetragonal crystal structure.

The combined findings of the above studies might allow the suggestion that there exists on the positive plate some poorly- (or non-) crystalline material that contains water and allows for a significant double-layer capacitance which is involved whenever the plate is exposed to high rates of charging. Simultaneously, much of the PAM is crystalline and is only able to accept charge, at non-extreme rates, by the traditionally accepted Faradaic reaction.

It should be noted here that promising hybrid supercapacitors have been produced with PbO₂ positive electrodes and conventional carbon negative electrodes. The successful development of the UltraBattery™ [19] with a PbO₂ positive plate and a negative that is partly sponge lead and partly carbon is also consistent with the conjecture that the capacitance of the plate can make a useful contribution to the storage of energy at high rates. With this novel design, the total discharge or charge current of the combined negative plate is composed of two components, namely, the capacitor current and the cell negative-plate current. Whereas fully-conventional batteries appear to require a periodic 'refreshing' charge in order to continue in successful operation, the UltraBattery™ has been demonstrated to operate for extremely long periods without any kind of conditioning operation [20]. Evidently, the capacitor electrode acts as a buffer to share current with the negative plate and thus prevent it from being discharged and charged at the full rates required in HEV duty.

In summary, energy may be stored in batteries by a capacitive process as well as by their Faradaic function. The former is available at much higher rates of charge and discharge than the latter, but the amount of charge that can be accommodated is limited by a linear dependence on potential.

6. Strategies for preventing sulfate accumulation and present successes

Lead–acid batteries should be specially designed to cope with the conditions that are encountered in HRPSoc duty. In particular, several factors are worthy of consideration in the development of an appropriate cell design to cope with the high rates that produce substantial gradients of local acid concentration and potential across the plate grid.

High-rate charge may be facilitated by:

- a negative plate with a high surface area that is electronically conducting
- the presence of an element in the active material of the negative plate that can absorb charge as capacitance
- the presence of a second phase that impedes the growth of lead sulfate crystals
- a grid design that allows potential to be as uniform as possible across the whole grid.

The first three of these perceived beneficial changes in cell design may be realized by the addition of three different types of additive to the negative plate. The programme of empirical development that has taken place in recent years, however, has indicated



Fig. 3. Honda Civic IMA in which the original nickel–metal-hydrate battery has been replaced with an UltraBattery™.

that different forms of one element—carbon—may perform the required functions adequately.

The two broad approaches to overcoming the problem of sulfate accumulation on the negative plate during HRPSoc duty are: (i) the incorporation of additional carbon in the negative active-material; (ii) appropriate grid design. Their efficacy has been individually demonstrated in a realistic way by the installation of batteries with the appropriate design features in two cars that draw heavily on the regenerative braking technology that is the principal cause of the abnormal mode of negative-plate failure.

The first project, in which the nickel–metal-hydrate battery in a Honda Civic IMA has been replaced by an UltraBattery™ of approximately equivalent capacity and voltage (Fig. 3), highlights the effectiveness of additional carbon in the negative plate of the lead–acid cell. The fuel economy of the UltraBattery™ Civic has been superior to that of the unconverted Civic during some of the drive cycles and little different in others, as demonstrated by the data presented in Table 3. The vehicle is currently in everyday use on the streets of Phoenix, Arizona, and continues to perform well after having completed 30,000 miles to date (May 2012).

An alternative approach to achieving sharply increased reductions in CO₂ emissions (and increase of fuel economy) is based on upgrading the performance of a base micro-hybrid. A plain micro-hybrid offering only stop–start functionality represents the least-expensive modification of a standard car design in pursuit of fuel economy but provides only a modest benefit. Mild- and full-hybrids yield greater reductions in CO₂ emissions, although at a much greater additional cost. Similar high reductions in emissions to those achieved in mild- and full-hybrids can be also be attained with low-voltage vehicles in which an efficient integrated starter/

Table 3

Comparison of fuel economies of Honda Civic IMA using a 168-V, 70-Ah Ultra-Battery™ and a Honda Civic IMA with the original nickel–metal-hydrate battery.

Drive cycle	UltraBattery™, mpg(US)	Unconverted Civic, mpg(US)
UDDS	61.7	53.1
Highway	59.8	61.0
US06	35.6	37.0
UDDS with AC on	49.8	36.0
Highway with AC on	45.9	47.7

UDDS: Urban Dynamometer Drive Schedule.

AC: air-conditioning.

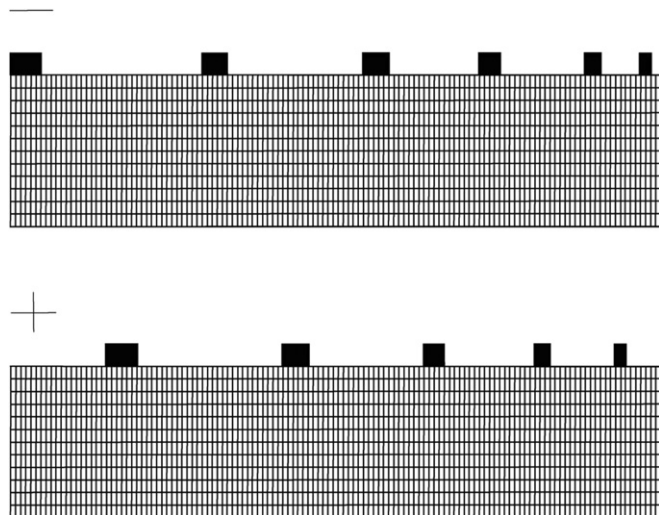


Fig. 4. Unrolled electrode grids (top: negative, bottom: positive) used in spiral-wound (cylindrical) lead–acid cell [10].

Table 4

Comparison of the performance of a VW *Passat* using a 12-V lead–acid battery, high-efficiency integrated starter/generator, and electric supercharger (*LC Super Hybrid*), with that of an unconverted *Passat*, and that of a Volvo *S40* which had a similar power rating to the *LC Super Hybrid*.

Features	Unconverted VW <i>Passat</i>	VW <i>Passat</i> LC <i>Super Hybrid</i>	Volvo <i>S40</i>
Engine volume, L	1.4	1.4	2.0
Power, bhp	122	142	145
Acceleration 0–100 km s ^{−1}	11.1	8.7	9.5
Fuel mpg (Imperial)	45.6	50.5	37.2
Liters per 100 km	6.2	5.6	7.5
CO ₂ g km ^{−1}	140	130	176

bhp = brake horsepower.

generator (ISG) collects regenerative energy and this, in turn, is used to power an electric supercharger. The vehicles are equipped with smaller engines than those in the normal, non-hybrid, versions and this downsizing results in substantial reductions of emissions. Normally the use of smaller engines would lead to some degradation in vehicle performance, but the additional presence of an electric supercharger makes good the otherwise-reduced power of the vehicle. The so-called ‘downsize and boost’ strategy produces a vehicle that provides the higher levels of fuel economy that will be required in the second round of emissions legislation, at a tolerable cost.

A project managed by the Advanced Lead–Acid Battery Consortium (ALABC) was devoted to the first exploration of the above advanced technology for micro-hybrids. The selected lead–acid battery had a spiral-wound design with multiple current tabs along the top edge of each of the positive and negative grids (Fig. 4) to reduce the heterogeneous distribution of potential. The findings of the project are summarized in Table 4. The performance of a ‘Micro/Mild’ vehicle—a VW *Passat*, labeled as ‘LC Super Hybrid’—is shown in the central column and is compared with that of an

unconverted VW *Passat* of similar engine size and with a Volvo *S40* that provides similar power. Clearly, the ‘Micro/Mild’ vehicle gives far more power, i.e., 142 bhp vs. 122 bhp, than the unconverted *Passat*. Furthermore, the CO₂ emissions are about 25% less than those from the Volvo *S40*.

The above two demonstrations of battery performance in vehicles serve to illustrate separately the effectiveness of two general strategies that cover the abovementioned four remedial approaches to sustaining HRPSoc service. The performance of the *Civic* shows the benefit of the carbon in the UltraBattery™, whereas that of the VW *Passat* demonstrates the benefit of the multiple connection tabs at the top of the plates.

7. Postscript

The need for improving fuel economy and reducing the emissions of the products of combustion from automobiles is widely accepted. The challenge is to meet these laudable aspirations at an acceptable cost. Fuel cell, plug-in hybrid electric and battery electric vehicles have all appeared initially to offer promise but, upon closer scrutiny, each retains some challenge in terms of cost and/or uncertain life-cycle emissions penalties. Nevertheless, strong interest continues in the commercial realization of proven, low-cost, technologies for sustainable road transport. Simple modifications to traditional designs of the lead–acid battery enable a low-cost route to the achievement of the necessary improvements in vehicle performance.

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